

# Fundamentals of negative ions

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# Outline

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- Formation and destruction of negative ions
- Applications
- Ball lightning
- Formation of plasmoids with sharply delineated edges in discharges
- Formation of ion-ion plasma in afterglow
- Anomalous conductivity due to droplets in metal vapors

# Periodic table (1/2)

## Electron affinity, $E_f$ , for negative ions

Group period	I	II	III	IV
1	H 0.75			
2	Li 0.62	Be 0.004*	B 0.28	C 1.2
3	Na 0.54	Mg 0.004*	Al 0.44	Si 1.4
4	K 0.5	Ca 0.02	Sc 0.19	Ge 1.2
5	Rb 0.49	Ba 0.15	Sr 0.11	Sn 1.1
6	Cs 0.47	Ra	Ba 0.15	Pb 0.36

# Periodic table (2/2)

## Electron affinity for negative ion formation

Group period	V	VI	VII	VII
1				He 0.075*
2	N 0.2*	O 1.45	F 3.4	Ne 0.095*
3	P 0.75	S 2.08	Cl 3.61	Ar 0.17*
4	As 0.81	Se 2.02	Br 3.36	Kr 0.65*
5	Sb 1.1	Te 1.97	I 3.06	Xe 1.25*
6	Bi 0.95	Po 1.9	At 2.8	Rn

Most elements including noble gases form negative ions!!!

Metastable negative ions life time ~0.5ms

# Applications of Plasmas Containing Negative Ions

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- **Common plasma:  $Te \sim 3\text{eV} \Rightarrow$** 
  - **negative ions in oxygen and halogens.**
    - Semiconductor manufacturing,
    - Negative ion sources,
    - D-layer in the lower ionosphere.
  
- **Colder Electrons,  $Te \sim 1\text{eV} \Rightarrow$** 
  - **negative ions in most other elements.**
    - $H^-$  negative ion sources

# Formation of negative ions

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- **Electron attachment**



energy,  $E_f$ , transfers to photons or third body

- **Dissociative attachment**



- **Charge transfer**

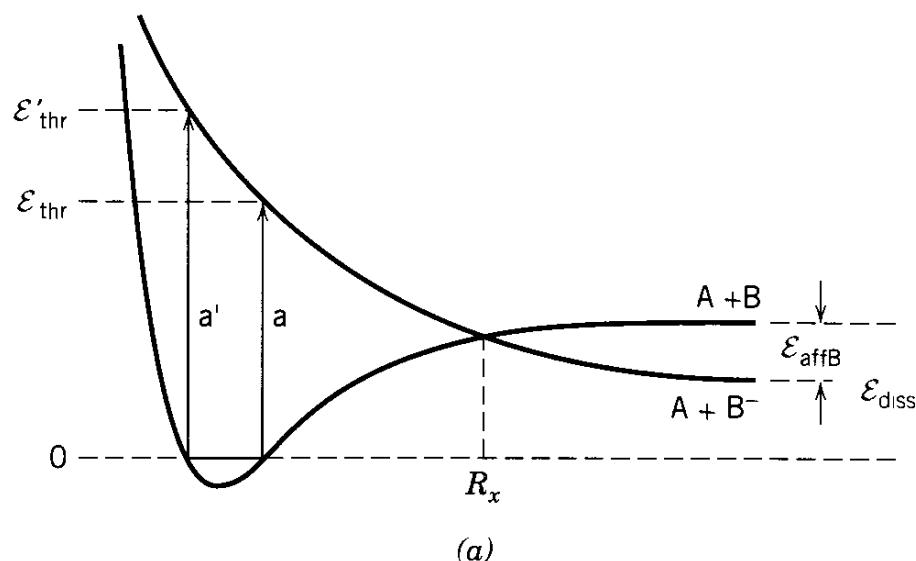


- **Clustering reactions**



# Dissociative attachment

**Potential curves of AB molecule and AB<sup>-</sup> negative ion as a function of inter-atomic distance.**



Electron with energy [ $E_{\text{thr}}$ ,  $E'_{\text{thr}}$ ] excites molecule, which with small probability dissociates into an atom **A** and a negative ion **B<sup>-</sup>**

And products are hot with energy  $E_e + E_{\text{affB}} - E_{\text{diss}}$   
Initial vibrational excitation can greatly enhance the attachment rate <sub>7</sub>

# Destruction of negative ions

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- **Electron detachment**



- **Associative detachment**



- **Charge transfer**



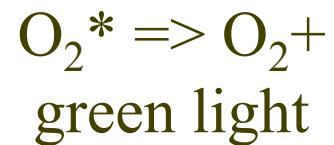
- **Positive-negative ion recombination**



# Long lived metastables are important

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The Nightglow as observed from Space. The lower left segment is the moon lit solid Earth, and the green arc above it is the Nightglow layer located about 100 km above the surface.



# Ball lightnings

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- Long lived
- Observed in presence of aerosols or dust => negative ions

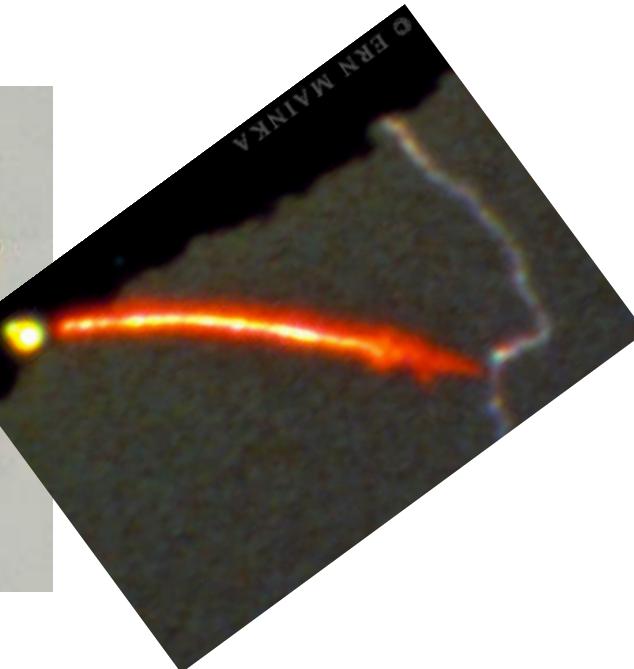


[www.zeh.ru/shm/index\\_e.php](http://www.zeh.ru/shm/index_e.php)

# Ball lightnings per Larry Grisham

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- lightning struck high-fidelity phonograph and repaired it.
- Larry's mother saw fire ball crossing the room



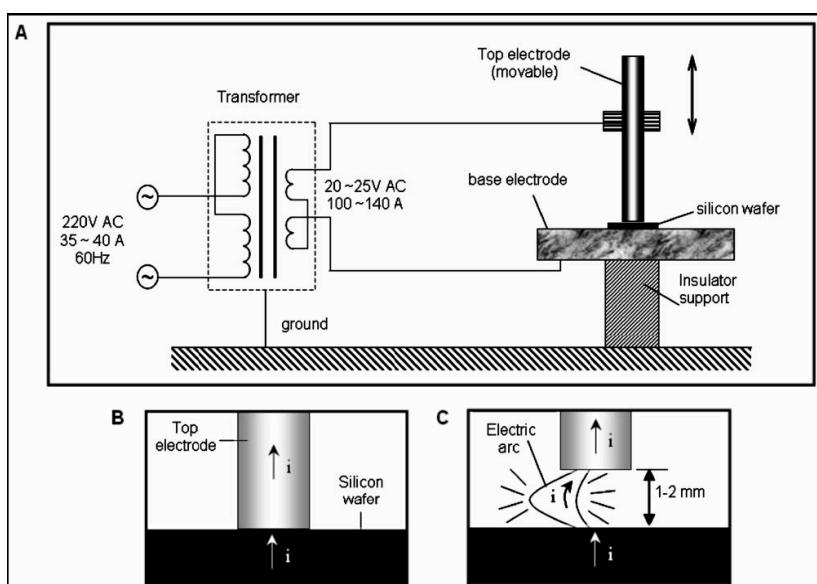
# Ball lightnings in laboratory (1)

- Eli Jerby and Vladimir Dikhtyar made lightning balls in the lab using a "microwave drill," *Phys. Rev. Lett.* 96, 045002 (2006).
- The energy from the microwaves then produces a molten hot spot in the substrate. The solid substrate is made from glass, silicon, or other ceramics.



# Ball lightnings in laboratory (2a)

- A Brazilian team made lightning balls in the lab using a dc arc, “*Phys. Rev. Lett.* 98, 048501 (2007).
- The energy from the arc produces silicon nanoparticles, which later burn.



# Ball lightnings in laboratory (2b)

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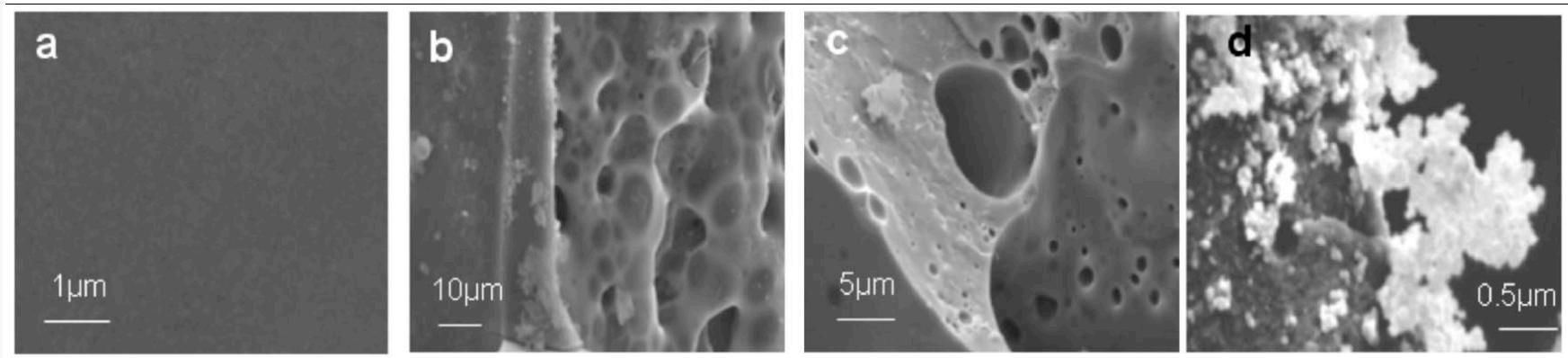
- Ball lightning goes under the cable



# Ball lightnings in laboratory (2c)

- The energy from the arc produces silicon nano-particles.

At the high temperatures created by the lightning strike, the carbon in the soil chemically reduces the Si oxides to the vaporized, metallic form of Si:  $\text{SiO}_2 + 2\text{C} \Rightarrow \text{Si} + 2\text{CO}$ . As the hot vapor cools in the atmosphere, the Si condenses into an aerosol of nanometer-sized Si particles in the air.



SEM of the Si wafer before (a) and after electrical discharge (b), (c), (d). The surface of the samples subjected to electrical discharges shows holes (b), (c) and chains of micrometer-sized particles (d).

Presence of negative ions produces many new nonlinear phenomena in gas discharge plasmas

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Ion density falls down precipitously -  
Negative ion density fronts

Nonlinear plasma decay in the afterglow

Ion density peaks near discharge periphery

Complex sheath structure

# Formation of plasmoids with sharply delineated edges in discharges

D. J. Economou, R. S. Wise, and A. A. Kubota,  
IEEE TPS 27, 60 (1999). Chlorine plasma of ICP.

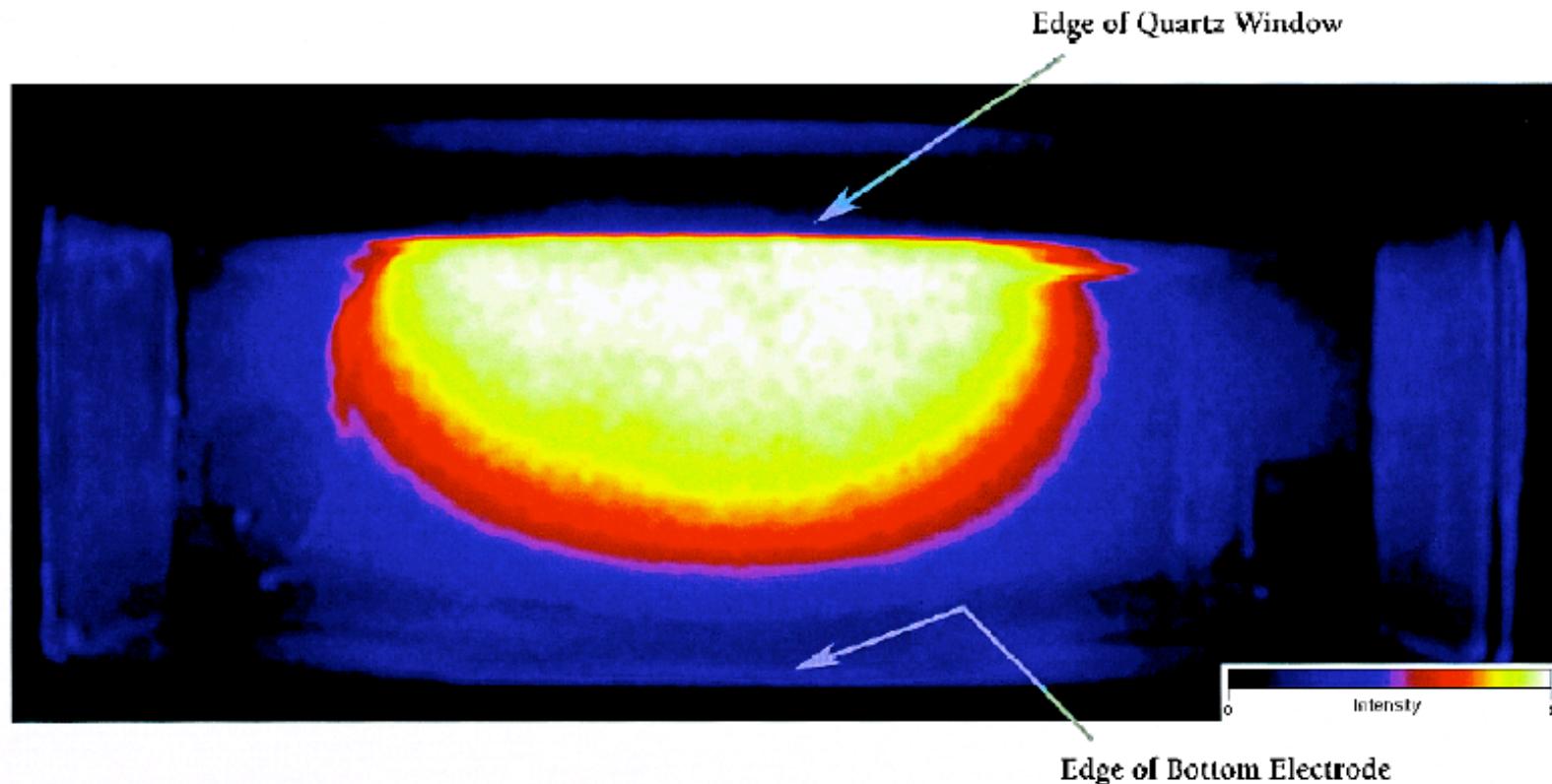
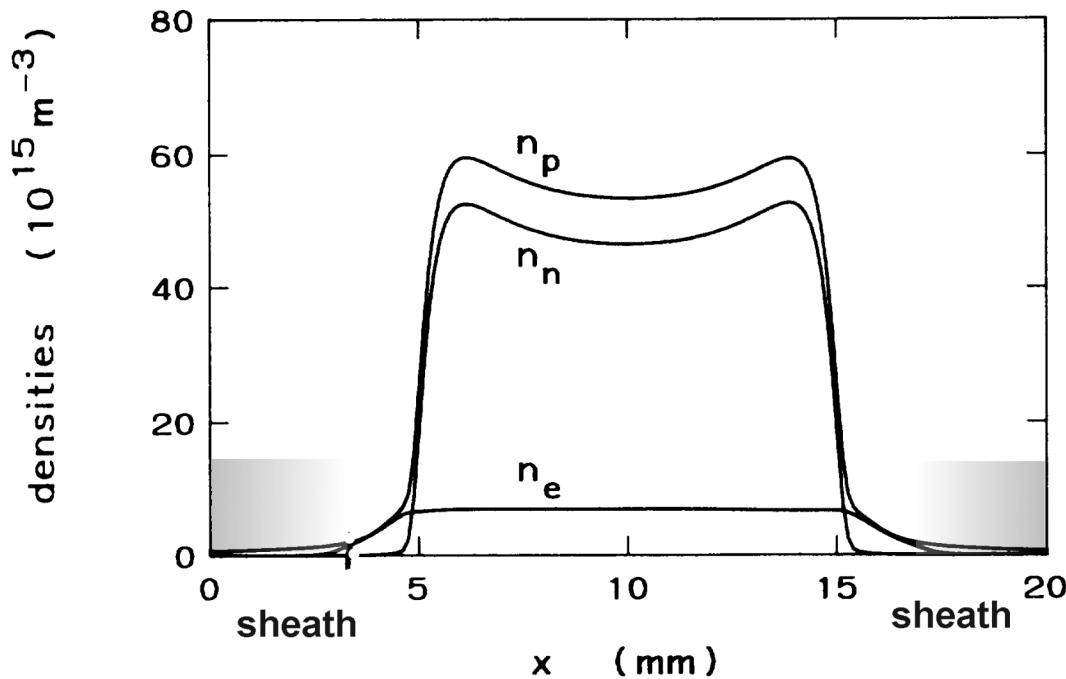


Fig. 1. Side view of a plasmoid formed at 5 mtorr. The bright structure is against the quartz window at the top and is well separated from the grounded bottom electrode. The spacing between the bottom electrode and the quartz window is 7.62 cm.

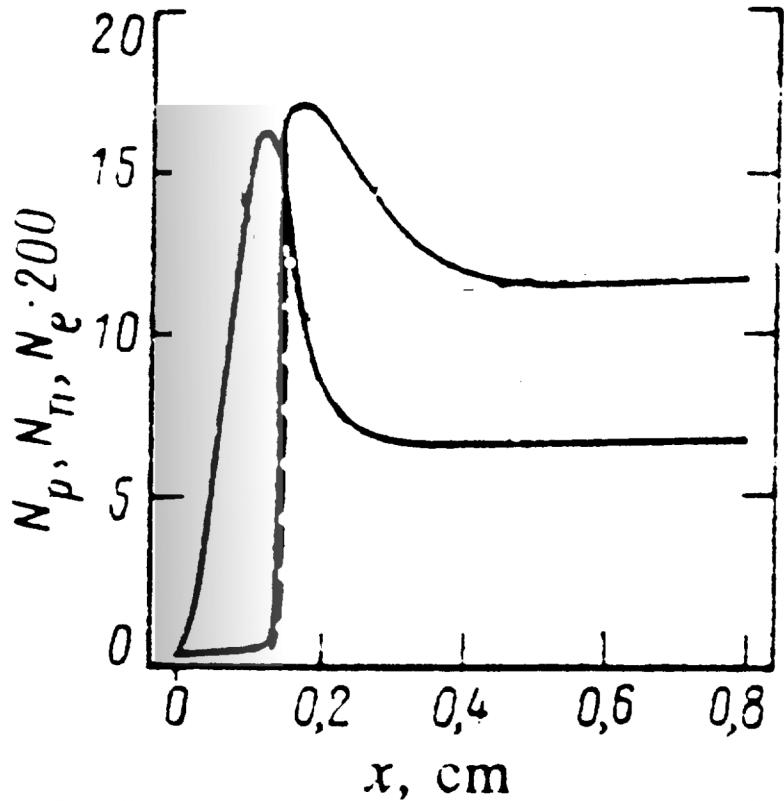
# The ion densities profiles exhibit discontinuities / simulation. (1/4)



**rf discharge,  
0.5 Torr CF<sub>4</sub>,  
13.6MHz.**

**Fronts form in  
the plasma  
bulk**

# The ion densities profiles exhibit discontinuities / simulation. (2/4)



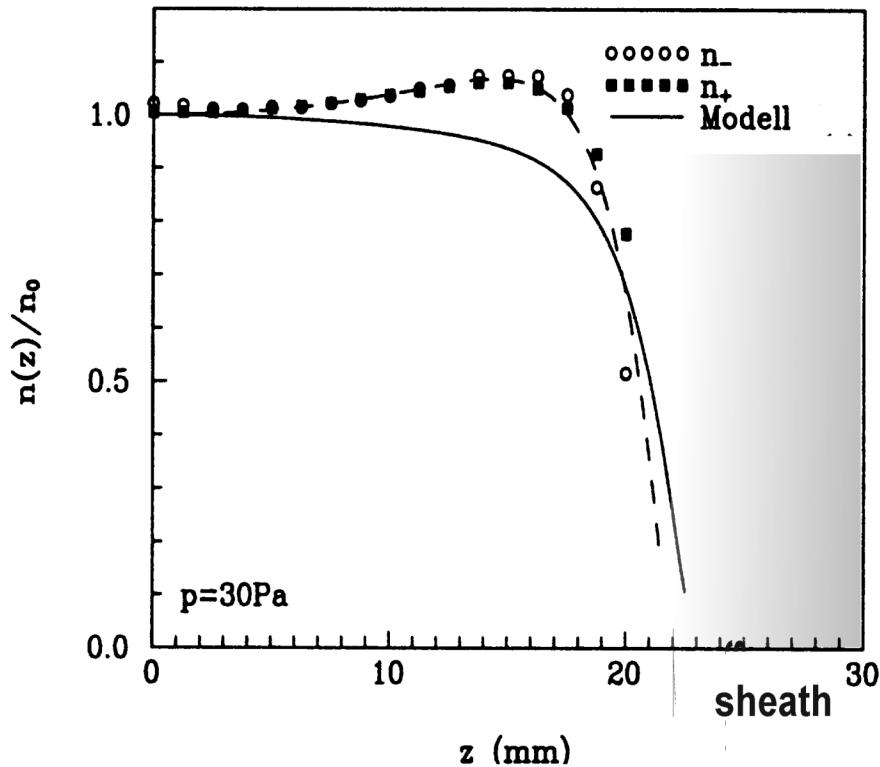
**rf discharge**  
**0.1Torr SF<sub>6</sub>**  
**f=13.56 MHz**  
**j=10mA/cm<sup>2</sup>**

**Fronts form at the  
sheath edge**

Simulation: V.A. Schveigert, Sov. J. Plasma Phys. **17**, 844 (1991).

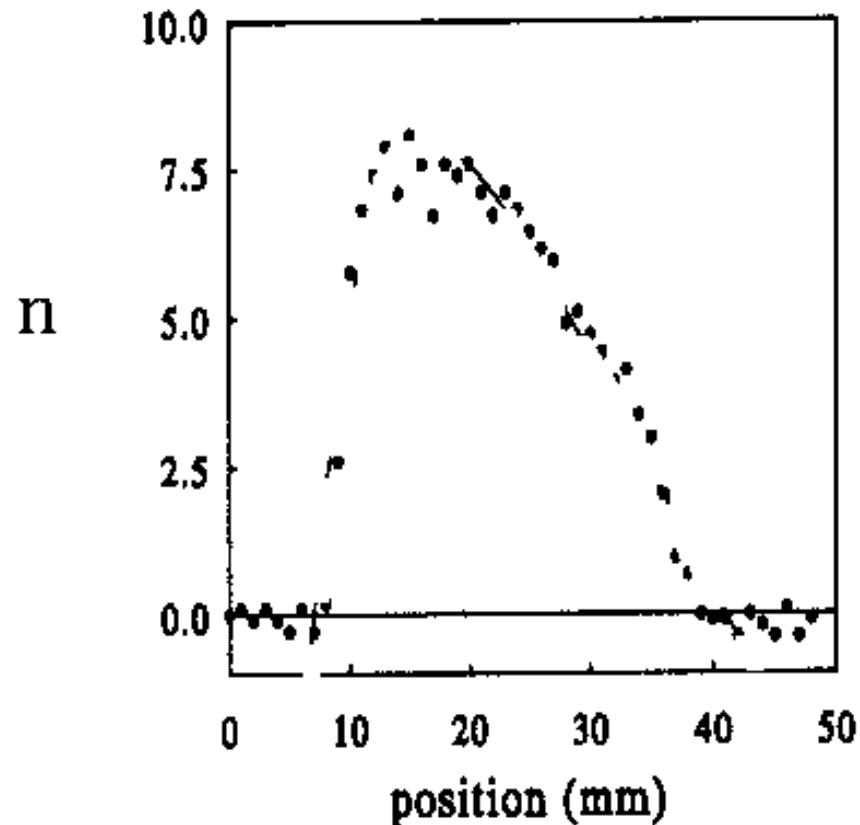
Theory: I.D. Kaganovich, Sov. J. Plasma Phys. **5**, 410 (1995). <sup>19</sup>

The ion densities profiles exhibit discontinuities / experiment. (3/4)



Symmetrical RF  
discharge CCP  
0.21Torr oxygen

The ion densities profiles exhibit discontinuities / experiment. (4/4)



**Asymmetrical RF  
discharge CCP  
100mTorr oxygen**

Dynamics of ion and electron densities is described by the drift-diffusion equations.

$$\frac{\partial n}{\partial t} - \mu \frac{\partial}{\partial x} \left( T_i \frac{\partial n}{\partial x} + eEn \right) = 0$$

$$\frac{\partial p}{\partial t} + \mu \frac{\partial}{\partial x} \left( -T_i \frac{\partial p}{\partial x} + eEp \right) = 0$$

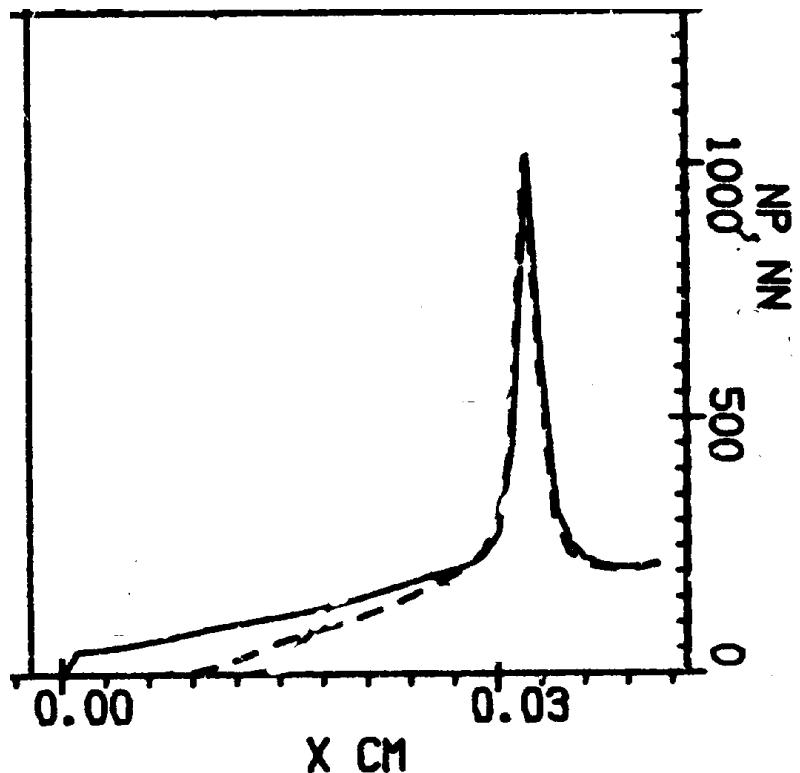
$$n_e = p - n \quad E = -\frac{T_e}{en_e} \frac{dn_e}{dx}$$

$$Ep = -\frac{T_e p}{en_e} \frac{dn_e}{dx} = -\frac{T_e (n_e + n)}{en_e} \frac{dn_e}{dx}$$

Ion mean free path is small => drift diffusion.

Here,  $p$ ,  $n$ ,  $n_e$  are positive , negative ion and electron densities.  $T_i$ ,  $T_e$  are the ion and electron temperatures,  $\mu$  is the ion mobility.

# Peaks of ion density in the sheath of the RF capacitively coupled plasma

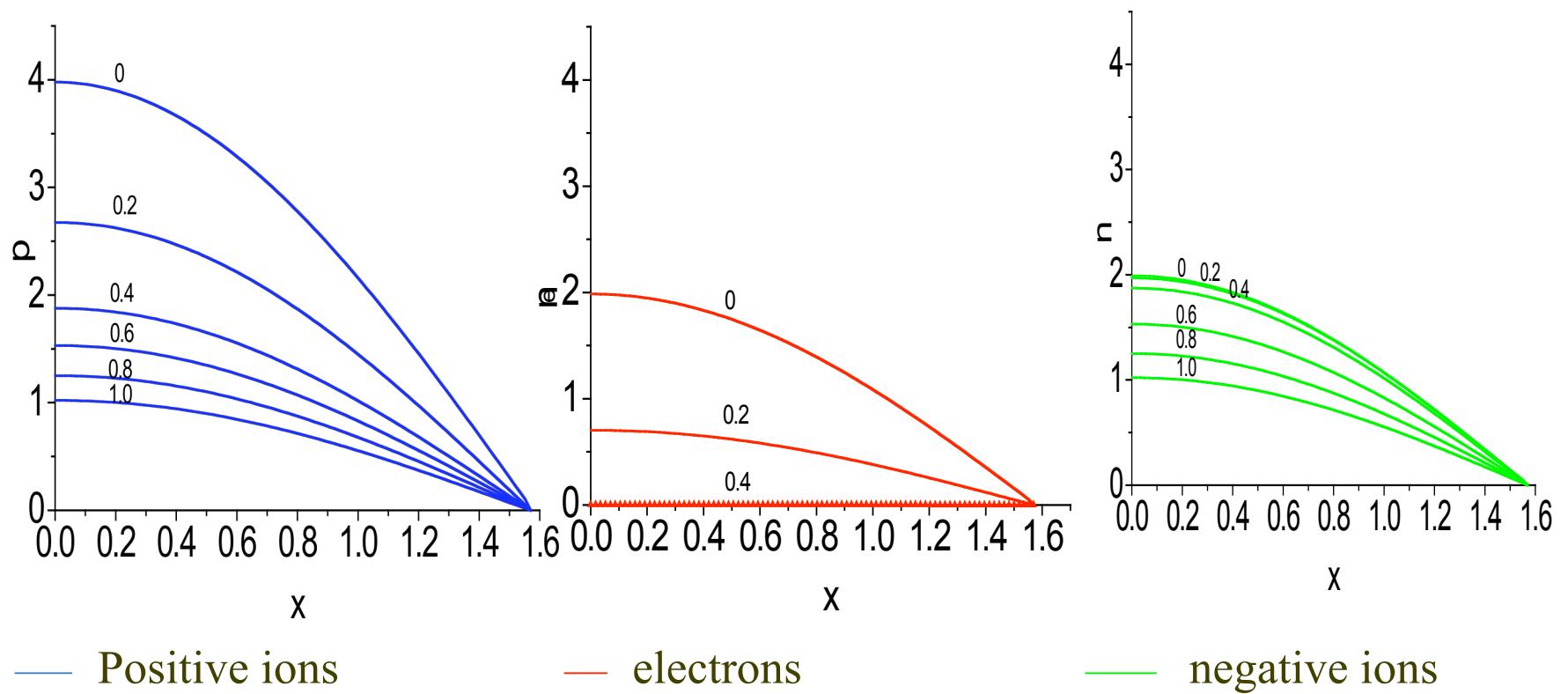


**Numerical simulation of  
a rf capacitive  
discharge in  $\text{SF}_6$ ,  
 $P=1 \text{ Torr}$ ,  $f=13.56\text{MHz}$ ,  
 $j=100\text{mA/cm}^2$**

Simulations: V.A. Schweigert Sov. J. Plasma Physics **17**, 844 (1991).

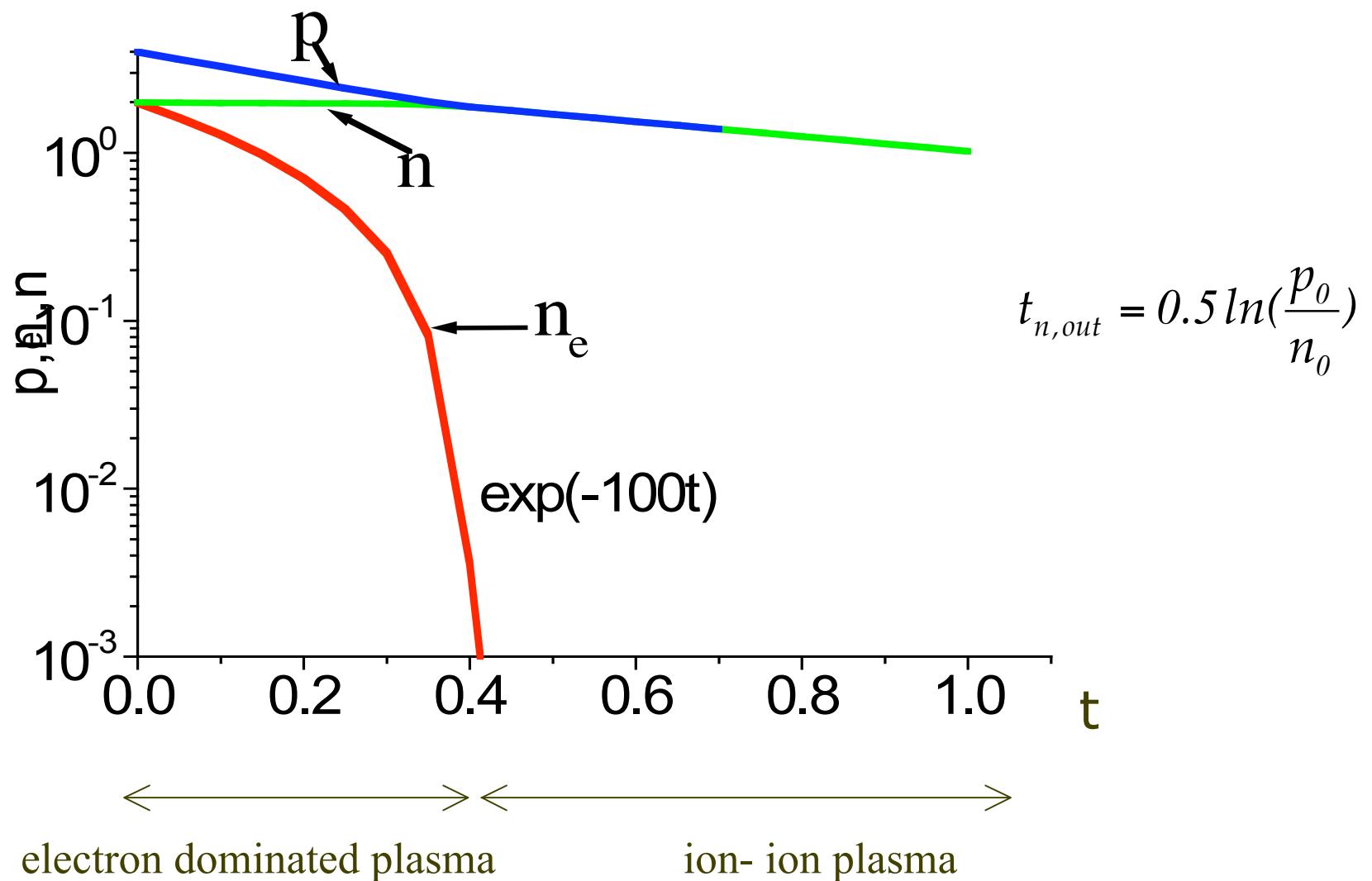
Theory: I.D. Kaganovich, Sov. J. Plasma Physics **5**, 410 (1995)<sup>23</sup>

# Formation of ion-ion plasma in afterglow: electrons can escape completely in finite time.

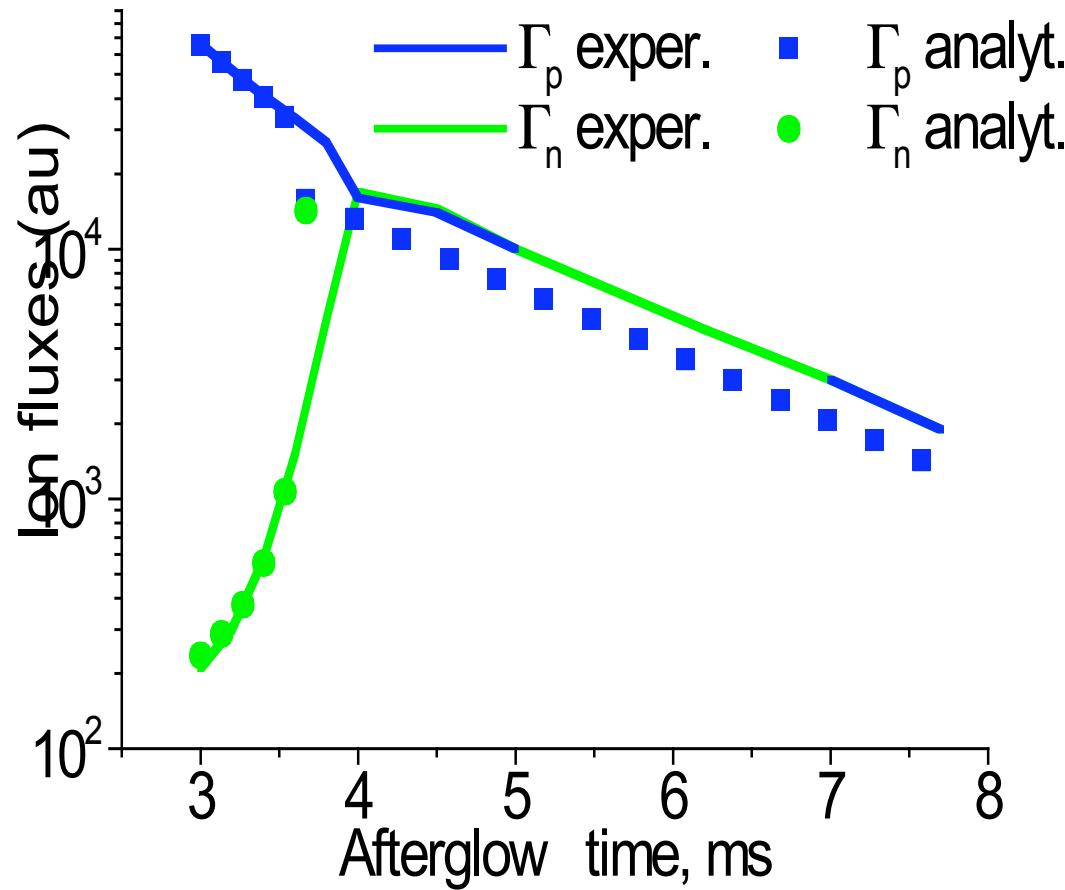


$T_e = T_i$ , wall losses only.  
Ions are present when electrons disappear.

# Electrons disappear in finite time.



# Negative ions flow to the wall after electrons disappear.



Experiment:  
Kr:O<sub>2</sub> 1:1 0.03Torr  
R=5.5cm, L=18cm

D.Smith, et al. J. Phys.  
D: Appl. Phys., 7, 1944  
(1974).

Theory:  
I.D. Kaganovich, et al. ,  
APL, 76, 284 (2000).

# Non-ideal plasma and negative ions

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**Ionization,  $\text{A} \leftrightarrow \text{A}^+ + \text{e}$**

$$\frac{n_e n_i}{n_a} = \frac{2\Sigma^+}{\Sigma} \left( \frac{m}{2\pi \hbar^2 \beta} \right)^{3/2} \exp(-\beta I),$$

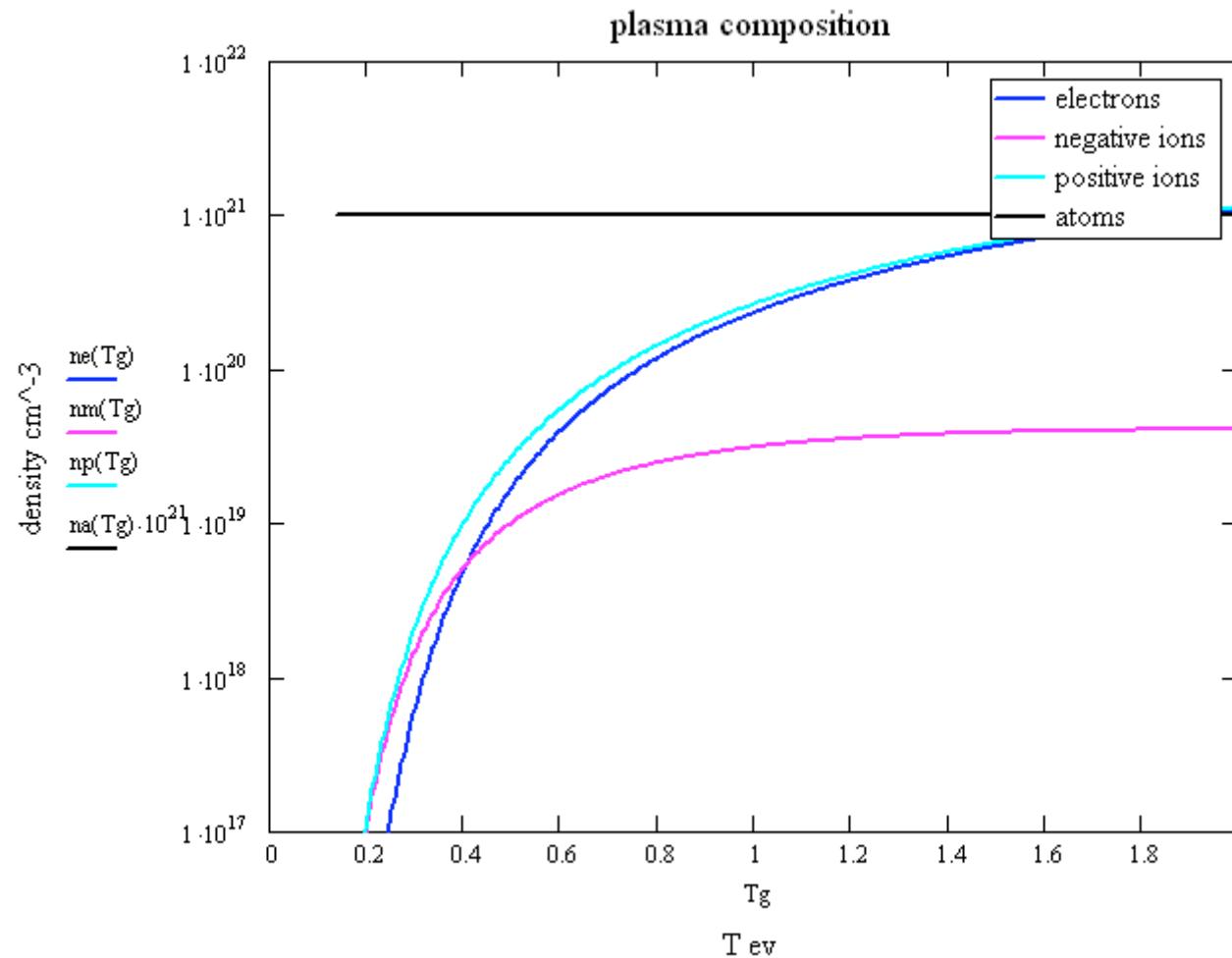
**Attachment,  $\text{A}^- \leftrightarrow \text{A} + \text{e}$ ,**

$$\frac{n^-}{n_e n_a} = \frac{\Sigma^-}{2\Sigma} \left( \frac{2\pi \hbar^2 \beta}{m} \right)^{3/2} \exp(\beta E).$$

$$\beta = 1/T$$

$$n_i = n_e + n^-$$

# Plasma composition for cesium

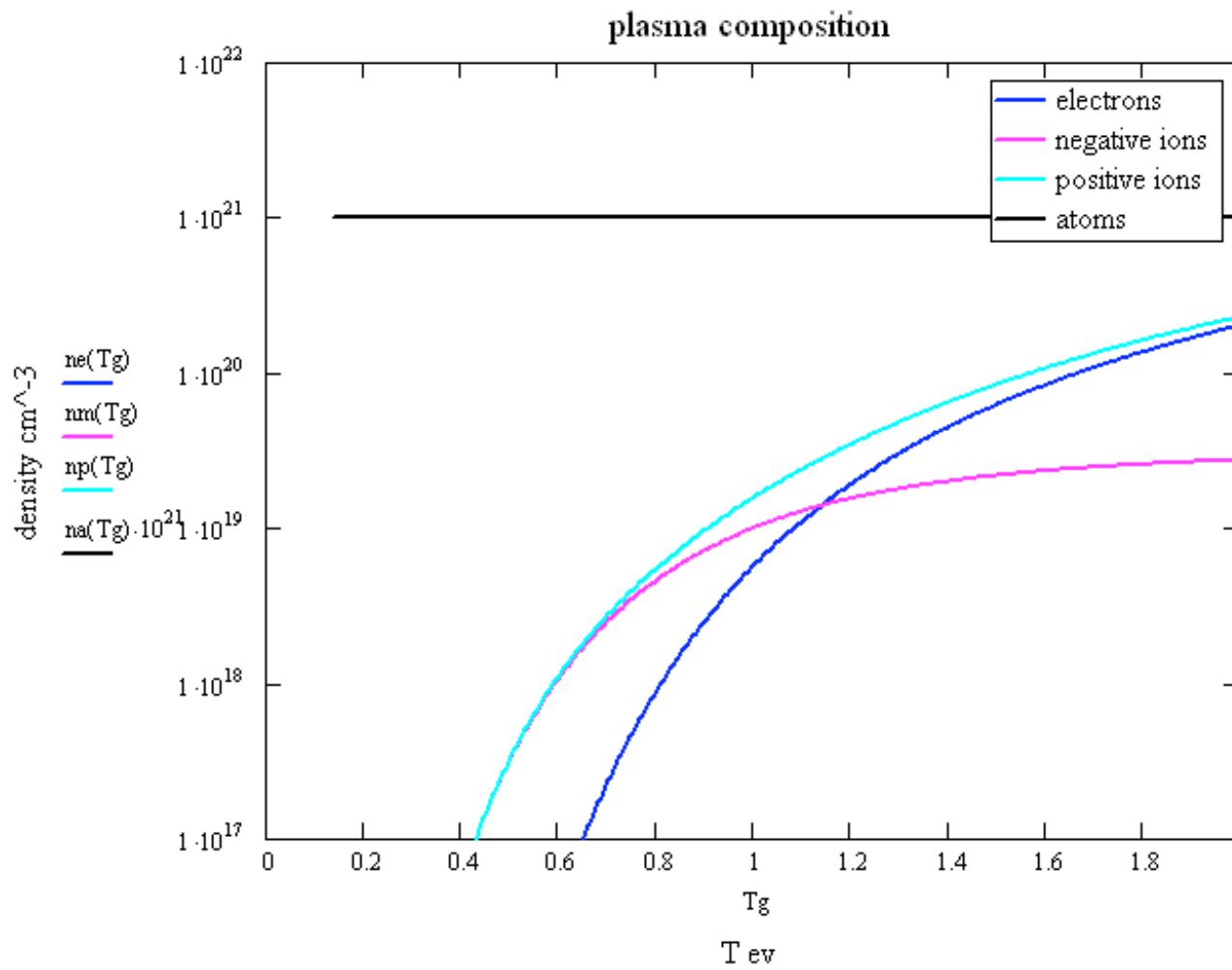


$$I = 3.09 \text{ eV}$$
$$E_{af} = 0.47 \text{ eV}$$

Ion-ion plasma  
at  $T < 0.4 \text{ eV}$ .

Formation of clusters has to be accounted for  $T < 0.2 \text{ eV}$ .

# Plasma composition for iodine



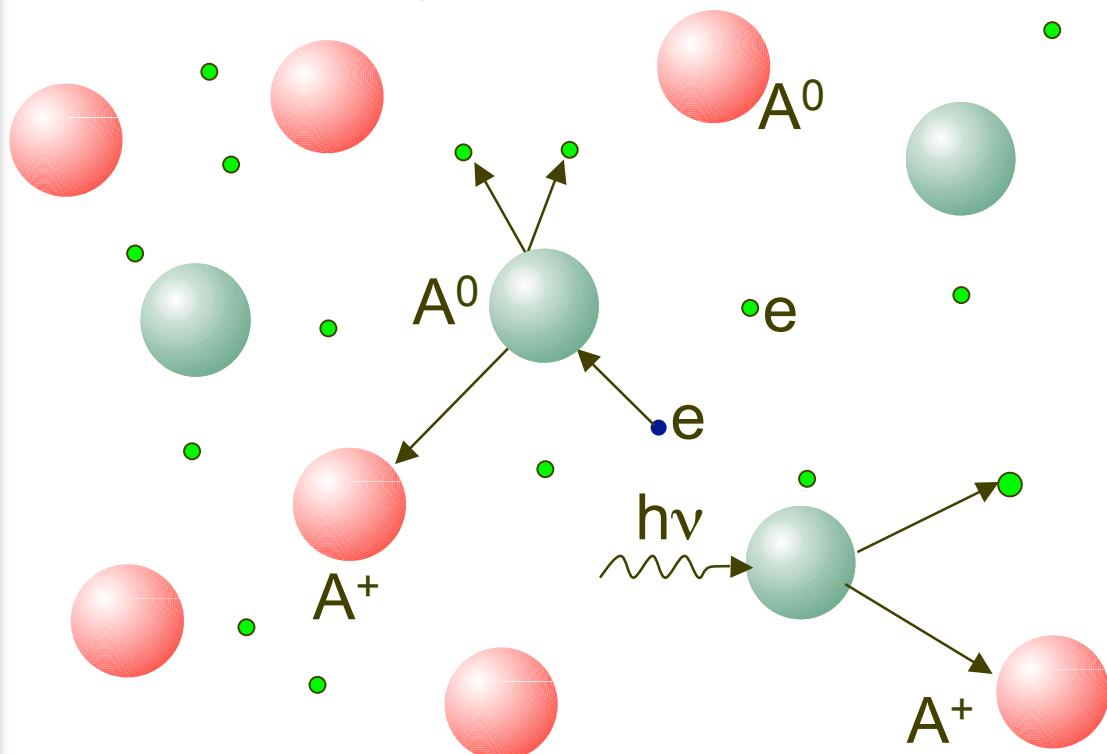
$$I = 10.45 \text{ eV}$$
$$E_{af} = 3.06 \text{ eV}$$

Ion-ion  
plasma at  
 $T < 1.1 \text{ eV}$ .

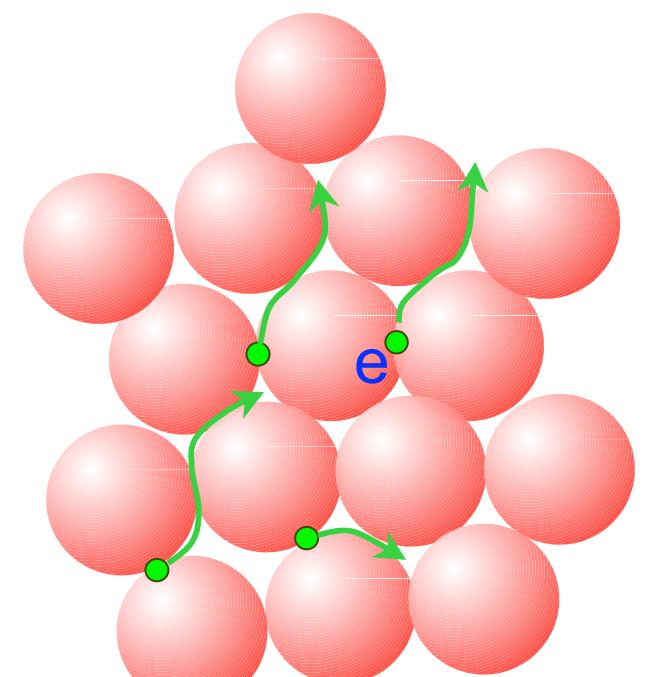
Formation of clusters has to be accounted for  $T < 0.2 \text{ eV}$ .

# Ionization in non-ideal plasmas

TEMPERATURE

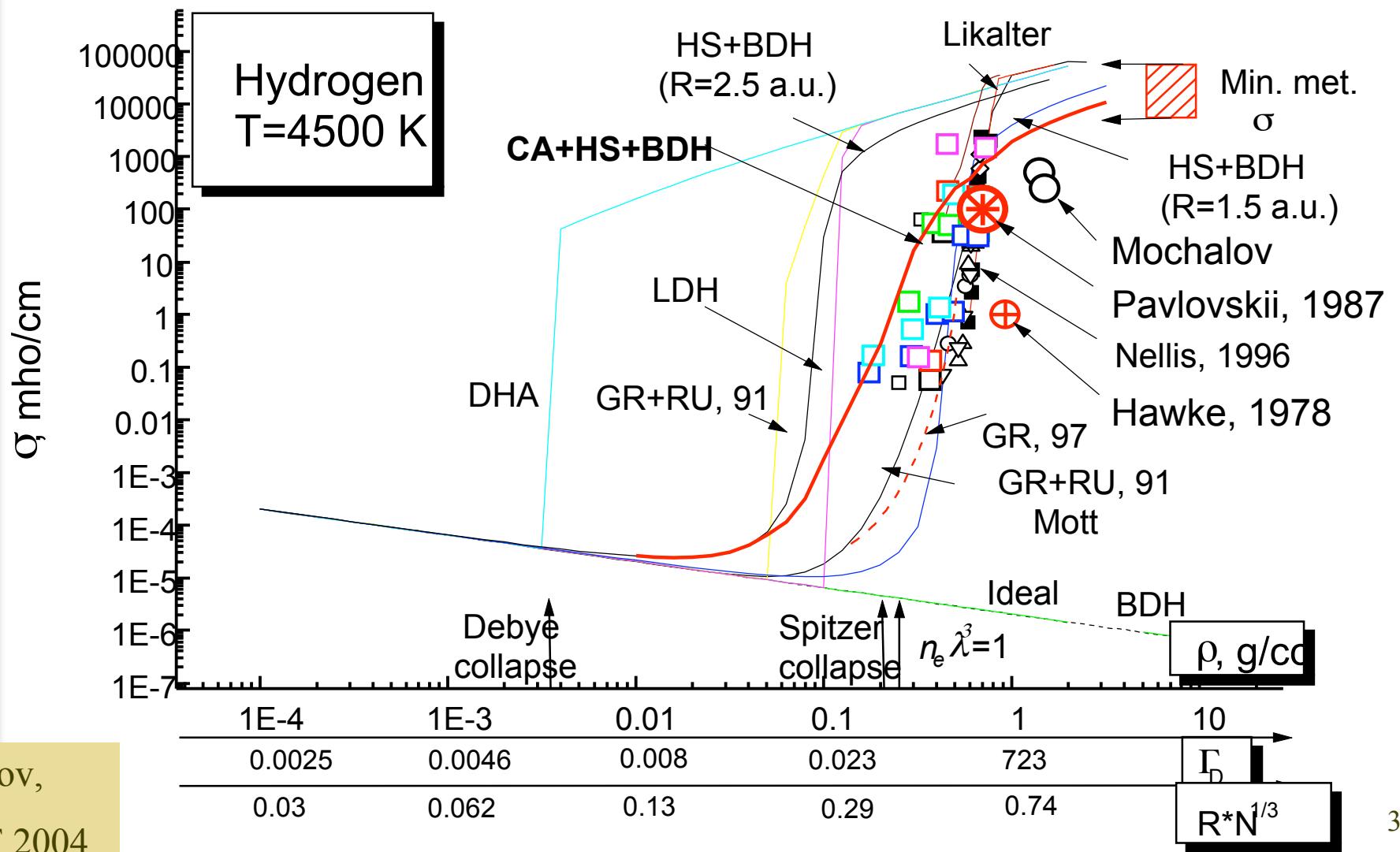


PRESSURE

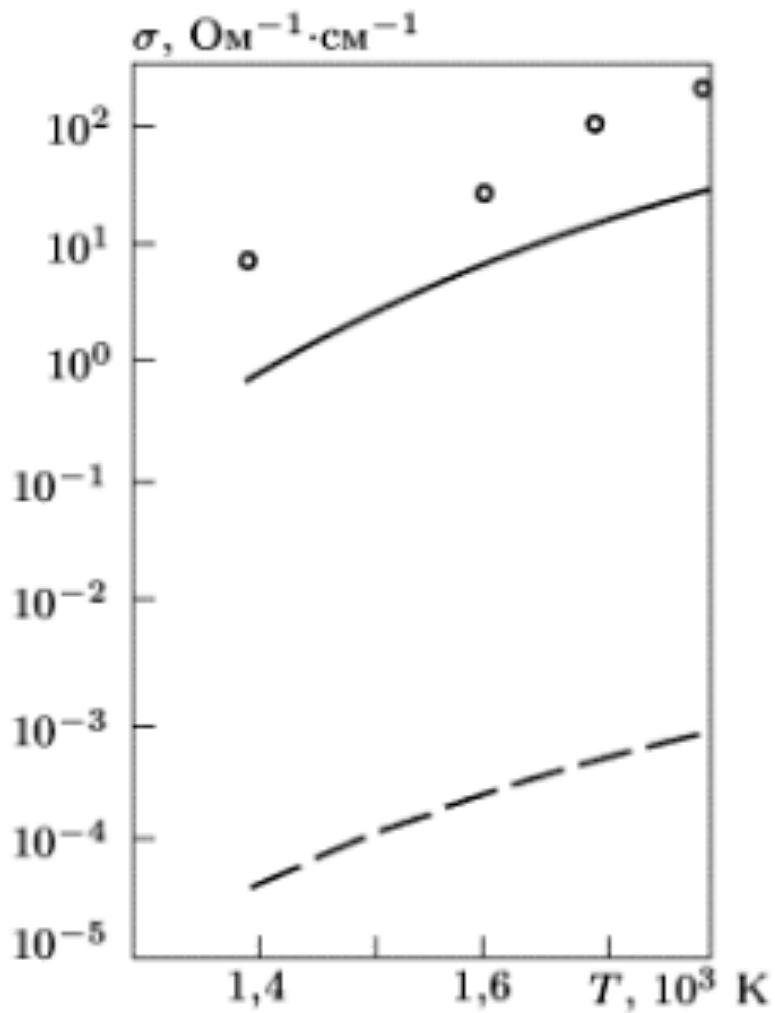


$$\text{Coulomb: } W_c \sim Z^2 e^2 n^{1/3}$$

# Hydrogen pressure ionization



# Anomalous Conductivity of Cesium



Conductivity of cesium vapor

Open dots – experiment

Dashed line - Saha equation

Solid line - droplet model

From Логосов В.В., Храпак А.Г. //  
ТВТ. 1988. Т. 26, № 2. С. 209-218.

# Summary (1/2)

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- Low temperature plasmas containing negative ions exhibit many nonlinear phenomena.
- Plasma separation in time and space into the regions with different ion composition is *universal property* of non-equilibrium plasma.
  - Concept of fronts has been successfully applied to plasma ignition, extinction and stationary state.

# Summary (2/2)

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- Formation of nanoparticles or droplets during melting and vaporization of solids may give rise to many new interesting phenomena like ball lightning and anomalous conductivity.
- Based on experience with discharges, negative ion WDM experiments may reveal new striking effects.

# Back-up explanatory slides

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# Analysis of Nonlinear Convection

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x}(un) = 0 \quad u = \mu T_e \frac{\partial \ln n_e}{\partial x} \quad \text{negative ion velocity}$$

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$$\frac{\partial n_e}{\partial t} - \frac{\partial}{\partial x}\left(D_{eff} \frac{\partial n_e}{\partial x}\right) = 0$$

$$D_{eff}\left(\frac{n}{n_e}\right) = \frac{\mu T_e(n_e + 2n)}{n_e}$$

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Electron effective diffusion coefficient

# Final Form: Nonlinear Convection

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$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x} u(n)n = 0$$

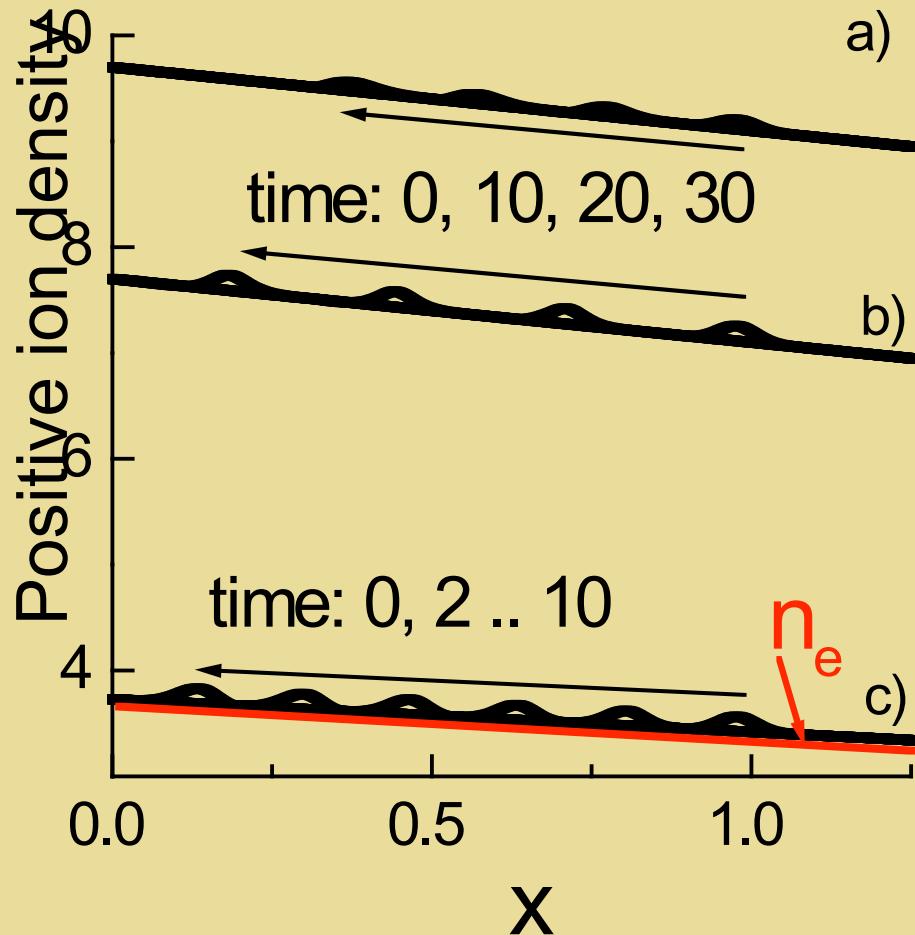
$$u(n) = -\Gamma_e \frac{\mu_n}{\mu_n n + \mu_p p}$$

$$\Gamma_e = -T_e \frac{\mu_n n + \mu_p p}{n_e} \frac{\partial n_e}{\partial x}$$

convective velocity is explicit function of density

electron flux is nearly conserved in narrow negative ion perturbations

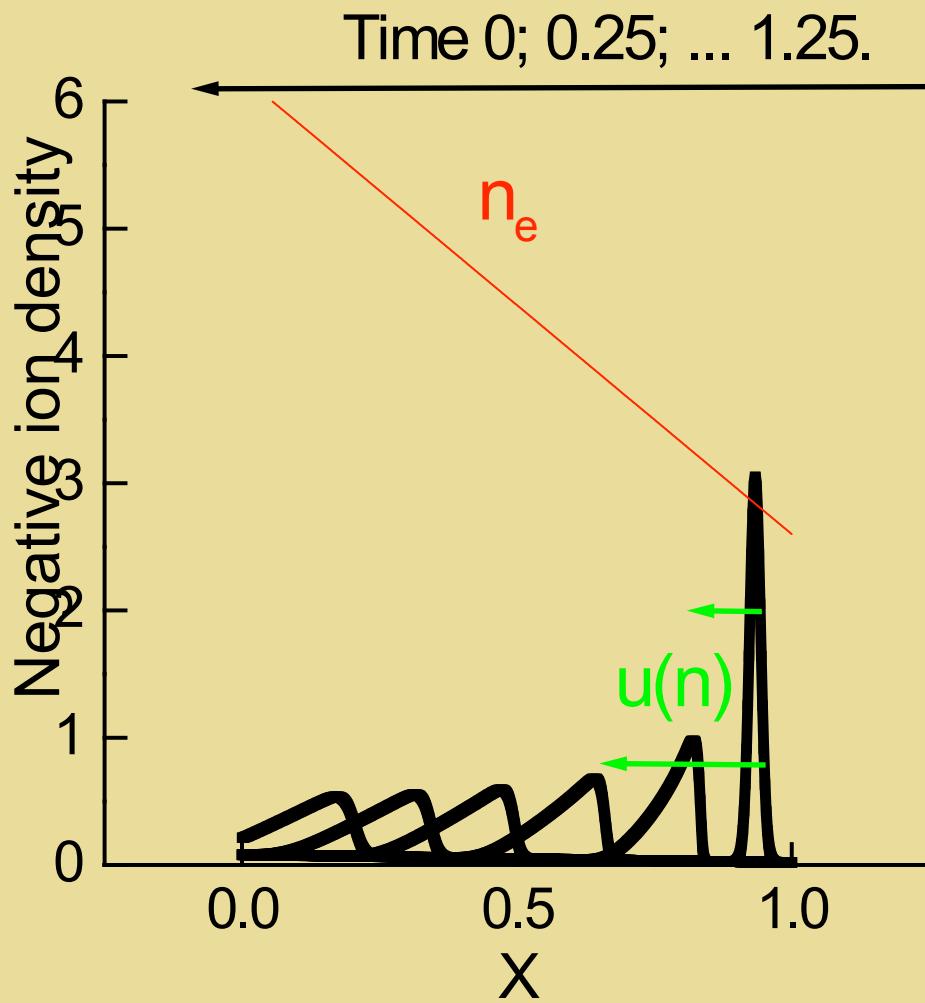
# Propagation of negative ion density depends on electronegativity $n/n_e$ .



- The same unperturbed electron density
  - ( $n_e = 3.7 - 0.3 x$ )
- Different electronegativity
  - (a)  $n = 6 - 0.3 x$ ,  $u_{\text{eff}} = 2.0$
  - (b)  $n = 4 - 0.3 x$ ,  $u_{\text{eff}} = 2.7$
  - (c)  $n = 0$ ,  $u_{\text{eff}} = 8.1$ .

$$u_{\text{eff}} = \frac{\mu_n \mu_p}{\mu_n n + \mu_p p} \frac{T_e \partial n_e}{\partial x}$$

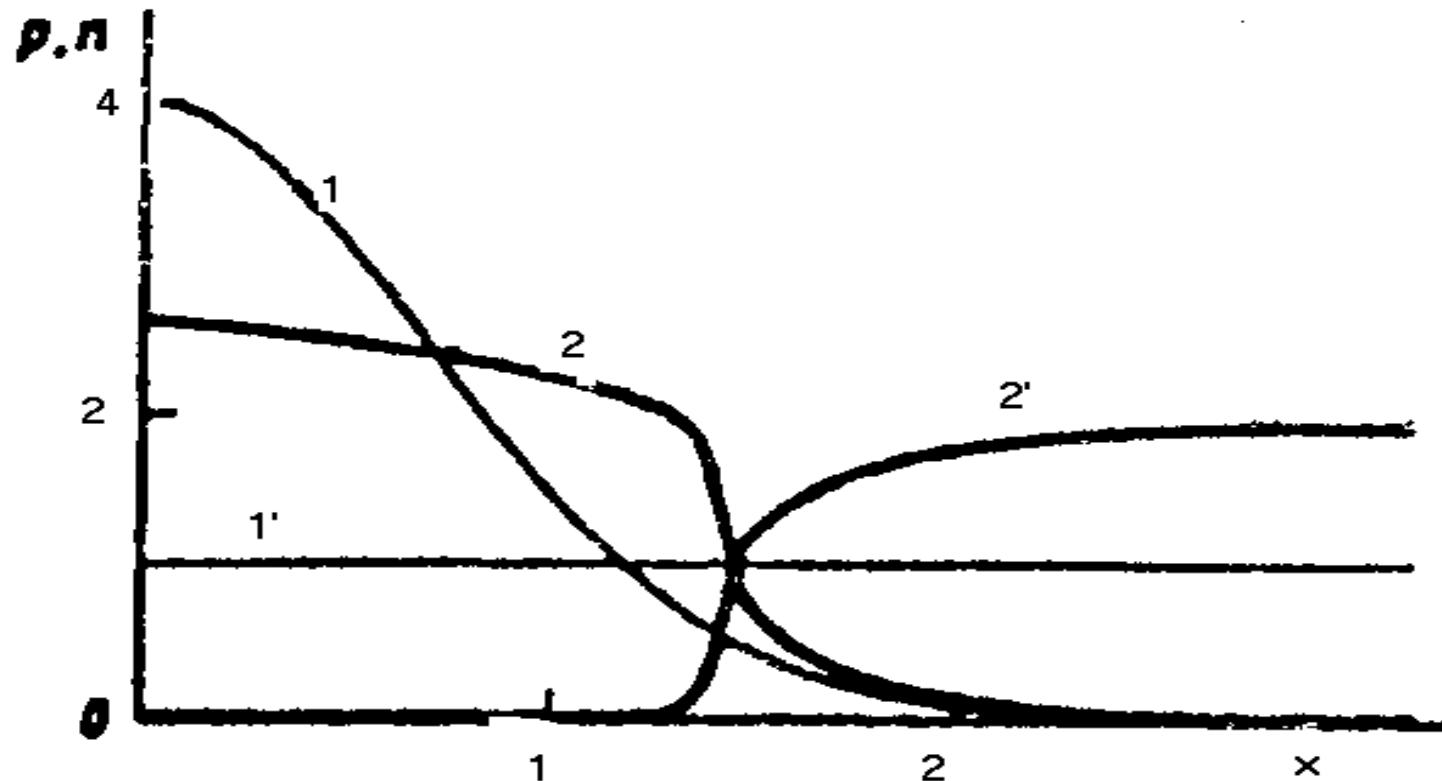
# Large perturbations deforms during nonlinear convection.



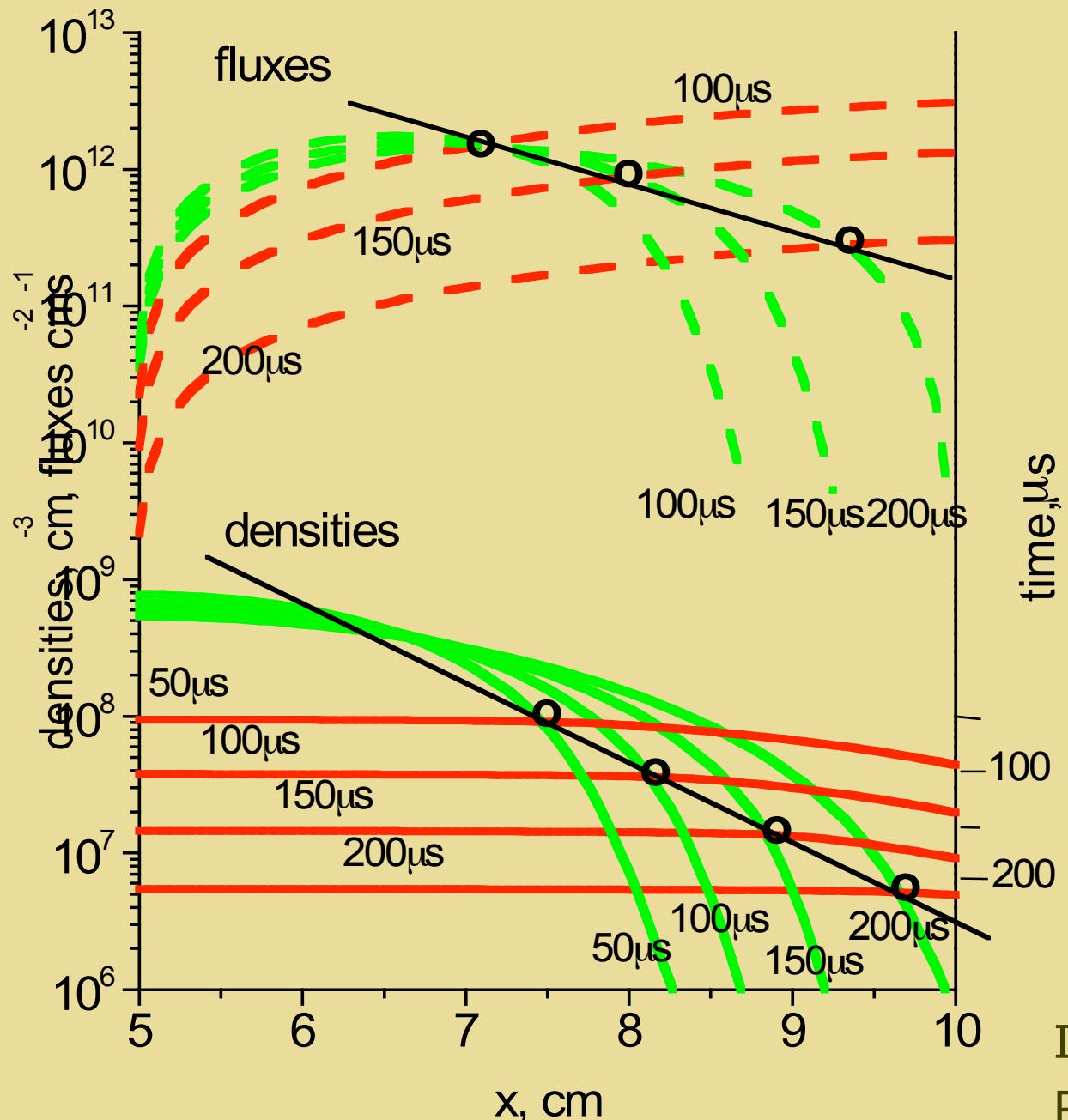
$$\frac{\partial n}{\partial t} + u_{eff}(n) \frac{\partial}{\partial x} n = 0$$

- Front profiles spreads,
- Back overturns

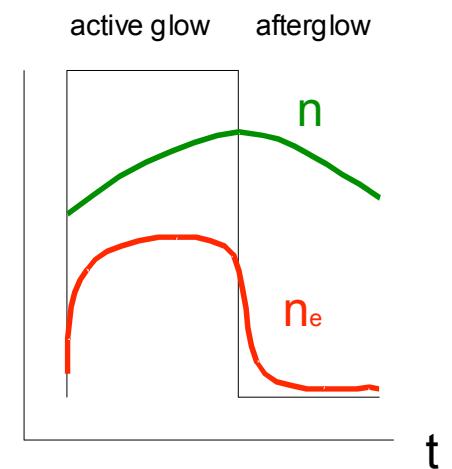
# Temporal Evolution, Self-separation of Positive Ions



1 -  $p(x)=4\exp(-x^2)$ , 2 -  $n(x)=1$  the profiles,  
1' and 2' corresponds to a time  $t=5$ ,  
the ratio of ion mobilities of 1 to 2 is 0.1.

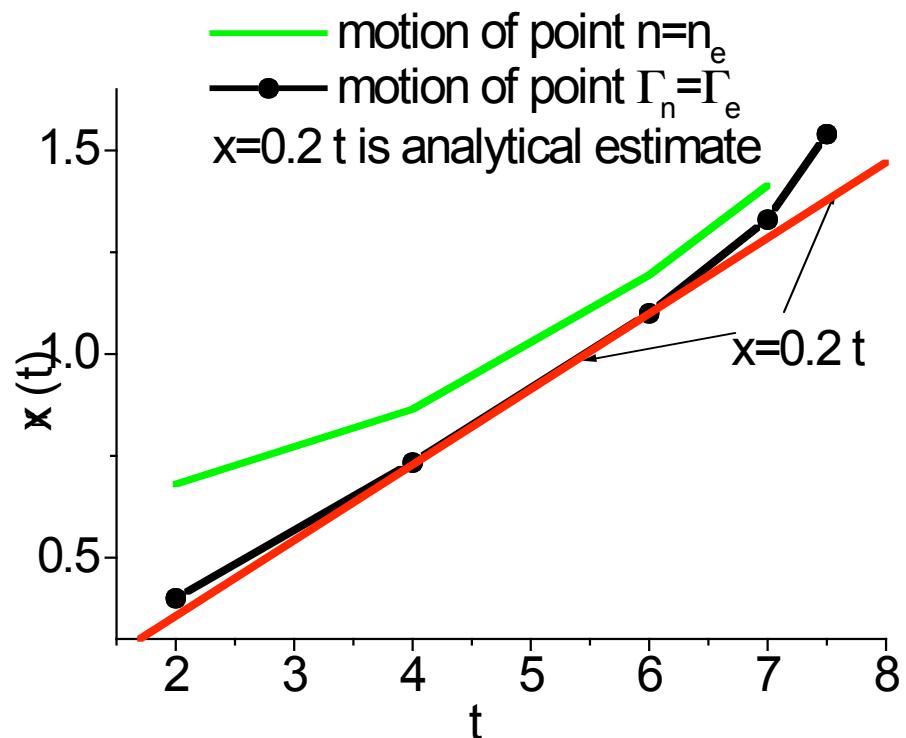


afterglow



I. Kaganovich, et.al.  
PRL **84**, 1918 (2000)<sub>41</sub>

# Motion of front in afterglow



Front is located at point  $x_{if}$  where  $n_e = n$

$$n(x, t) = \frac{N}{\sqrt{4\pi D_i \tau}} e^{-\frac{x^2}{4D_i \tau}}$$

Free ion diffusion with diffusion coefficient  $D_i$

$$n_e(t) = n_{eo} e^{-Z_{e,loss} \tau}$$

$Z_{e,loss}$  is electron loss frequency.

$$\frac{x_{if}^2(t)}{4D_i \tau} = Z_{e,loss} \tau$$

Small amount of electron density determines the electric field.

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currentless plasma:

$$j = e(\Gamma_p - \Gamma_n - \Gamma_e) = 0$$

$$eE = \frac{-D_e \nabla n_e - D_n \nabla n + D_p \nabla p}{\mu_e n_e + \mu_p p + \mu_n n}$$

$$n_e \mu_e \gg (\mu_p p + \mu_n n)$$

$$n_e \mu_e \ll (\mu_p p + \mu_n n)$$

- **electron dominated plasma**

$$E = -\frac{T_e}{e} \frac{d \ln(n_e)}{dx}$$

- **ion-ion plasma**

$$\text{if } \mu_p = \mu_n \ E = 0$$

# Afterglow, role of electron production

## (1/3)

- If enough electrons are present
- negative ions are trapped
- negative ion flux is small

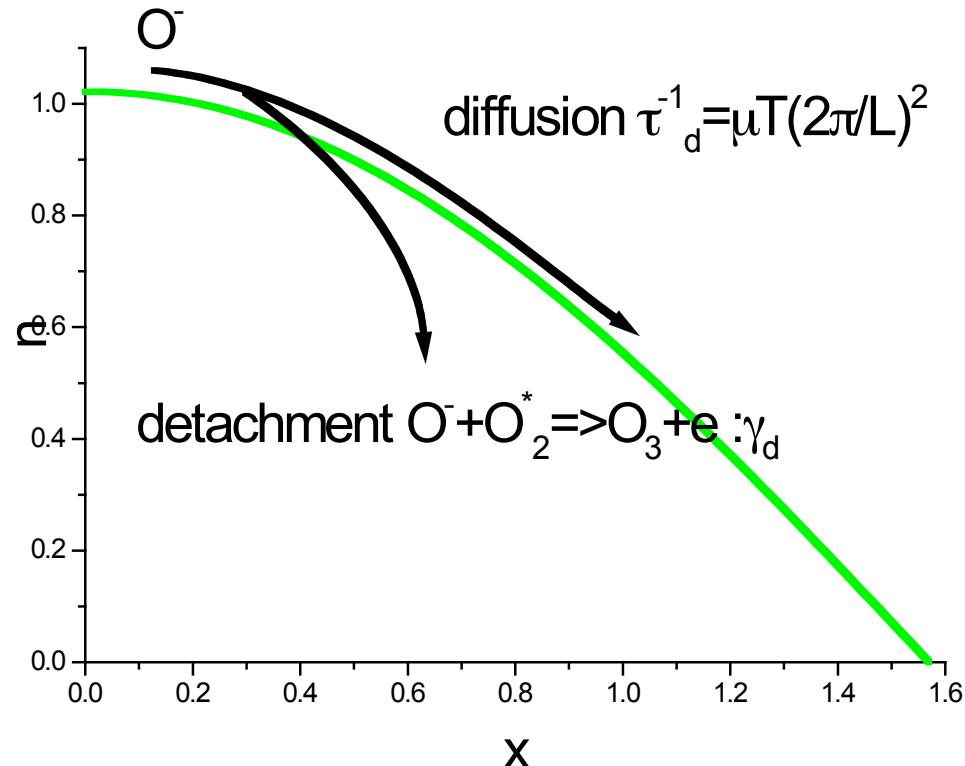
$$E = -\frac{T_e}{e} \frac{d \ln(n_e)}{dx}$$

$$\Gamma_n = -D_n \frac{\partial n}{\partial x} + \mu_p n E \approx 0$$

$$\Gamma_n \approx 0$$

electron production in afterglow  
may result in negative ion trapping

If negative ion are destroyed during the diffusion to the wall, negative ion flux at the wall vanishes (2/3)

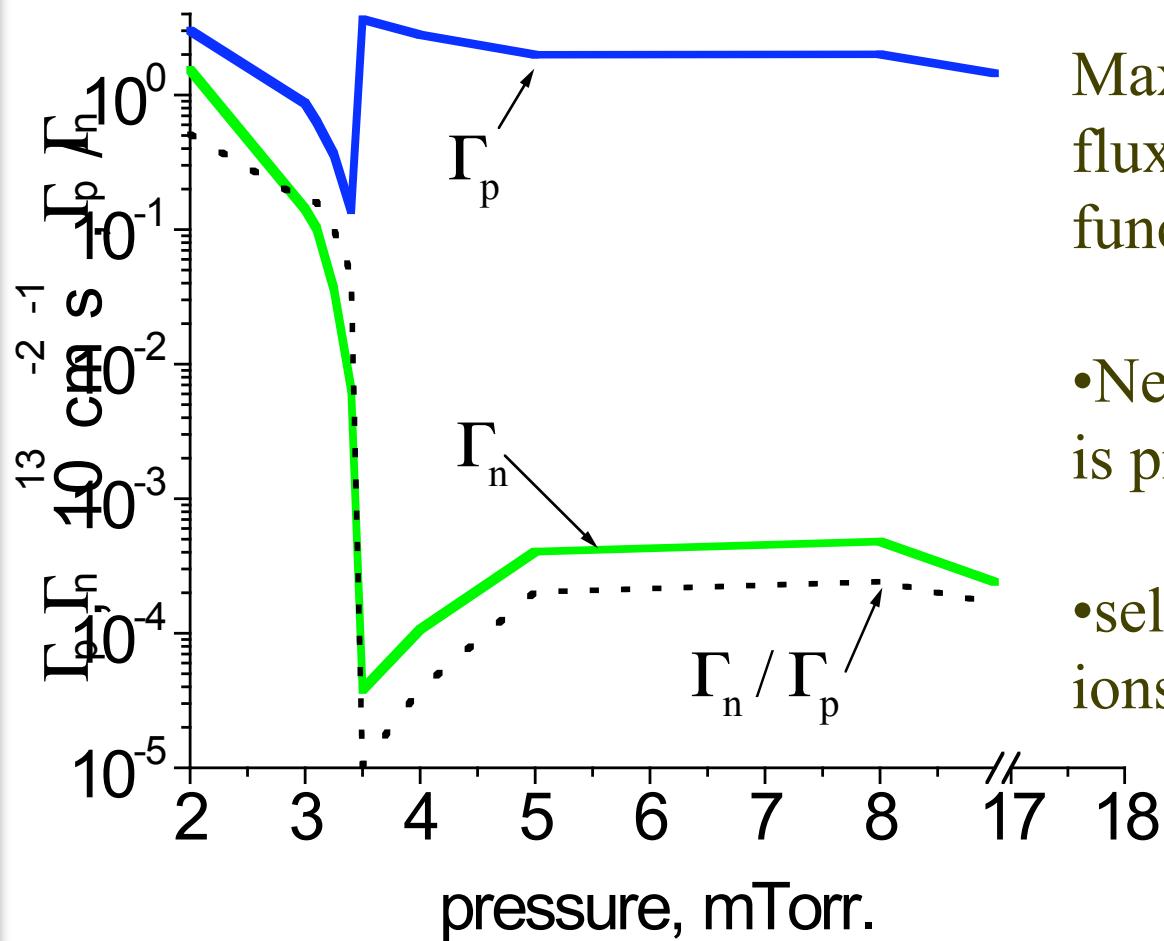


Electron productions  
⇒ Electric field  
⇒ Trapping of ions

Turning point

$$\gamma_d \frac{(2L)^2}{2\pi^2 \mu_i T} \equiv \gamma_d \tau_d / 2 = 1$$

# Bifurcation of negative ion flux as function of pressure (3/3)



Maximum of negative ion flux in the afterglow as function of pressure.

- Negative ion detachment is proportional to pressure
- self-trapping of negative ions at higher pressures

I.D. Kaganovich, et al.,  
APL, 76, 284 (2000).